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High Performance Nanostructured Ni-Mn Alloy for Microsystem Applications

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A process has been developed for the electrodeposition of a high strength, heat resistant Ni-Mn alloy for high aspect ratio microstructures (HARMST). A conventional Ni sulfamate electrolyte is employed with the addition of a small amount of manganese chloride. The deposits are low stress ($< \sim 60$ MPa tensile), enabling the deposition of thick section films required for HARMST. The Mn content for the alloys of interest is less than about 1 wt %, and its codeposition is insensitive to mass-transport effects, permitting uniform alloy deposition, regardless of feature aspect ratio. A pulsed deposition scheme is employed to fabricate a nanostructured film consisting of alternating nanometer thick regions of relatively pure Ni, and hard, Mn-rich Ni; this moderates the high stress of the NiMn alloy and enables the deposition of thick deposits. Yield strengths of over 800 MPa are achievable, with good as-plated ductility (~6%). The material loses only about 15% of its original strength after a 1 h, 600°C anneal, and no embrittlement is observed since no S-bearing additives are employed.
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Electrodeposition through thick photoresist (such as SU8 or polymethylmethacrylate [PMMA]) has enabled the fabrication of high aspect ratio (*i.e.*, large height-to-width ratio) metallic microstructures (HARMST) for various applications.[1-5] A review of through-mask electrodeposition can be found in Ref. 5. The electrodeposited metal of choice is nickel, typically deposited from a sulfamate bath. However, for some applications, the strength of the as-plated Ni is insufficient. As the cross-sectional areas of microfabricated components decrease (to save space and weight, for example), the stresses experienced in load-bearing members (*e.g.*, actuators, springs, flexures) necessarily rise.[6] Relatively soft electrodeposited metals such as Ni from a sulfamate bath ($\sigma_y \approx 350$ MPa) are hence of little use where high strengths are required.

High strength in electrodeposited materials results principally from grain refinement. Grain-refining additives, such as saccharin, produce fine-grained, hard, and high strength Ni. We have employed them to achieve strengths comparable to those in the literature.[7] Although convenient, the use of such additives typically contributes hundreds of ppm of sulfur to the deposit; the sulfur migrates to the grain boundaries upon annealing, causing catastrophic embrittlement and intergranular fracture.[8] In practice, sulfur incorporation is difficult to predict and control.[9-11] Because the possibility of sulfur embrittlement and catastrophic failure is unacceptable for many if not most of our applications, this approach to increasing strength was abandoned.

Electrodeposited NiCo alloys are similarly fine grained (for Co concentrations of about 30%), have high strength, and have been deposited without S-bearing, stress-relieving additives.[7] But Co codeposition rates are highly dependent on local mass-transfer conditions,[12] and because mechanical properties of these alloys are directly related to Co content, unacceptable variations in alloy composition and strength occur as feature depth and aspect ratio increase. This may be overcome to some degree by pulse plating, but in our experience with typical electrolyte formulations and pulse parameters designed to achieve uniform alloy composition, deposition rates were unacceptably low. Moreover, we found that, in agreement with literature results, alloy compositions having high yield strengths showed high intrinsic stress.[7] This leads to the delamination of the plated microparts from the substrate, rendering them useless.

We describe in this communication a process for the electrodeposition of a high strength Ni-Mn alloy that obviates these problems. Electrodeposited NiMn alloys have been studied before, but their high stress levels complicated their implementation as thick deposits.[13-15] We solve this problem by nanostructuring the alloy with pulsed deposition to moderate plating stresses. As NiMn can be uniformly deposited in thick sections independent of feature aspect ratio, it should be useful for producing more complex structures comprised of a number of different feature sizes.

Experimental

A PAR 273 potentiostat in galvanostatic mode was used for all electrodeposition. The reactor for sample preparation was a 10 L glass cell; a circulation pump (Floking, FL) with a 5 μm filter provided agitation in the cell and across the wafer face, while a temperature controller (Cole-Parmer) kept the reactor temperature at 28 ± 1°C unless noted otherwise. A bagged, titanium anode basket with nickel S-rounds (Inco, Canada) served as a counter electrode in a two-electrode arrangement. The pH was kept between 3.5 and 4.0; in a previous study of NiMn deposition, the pH had a negligible effect on the Mn codeposition rate.[13] The electrolyte was 1.35 M Ni-sulfamate (Atotech, Germany), 30 g/L boric acid, and 0.2 g/L sodium dodecyl sulfate. Mn was added as $MnCl_2 \cdot 4H_2O$; all chemicals were ACS grade from Aldrich unless otherwise noted. Mn elec-

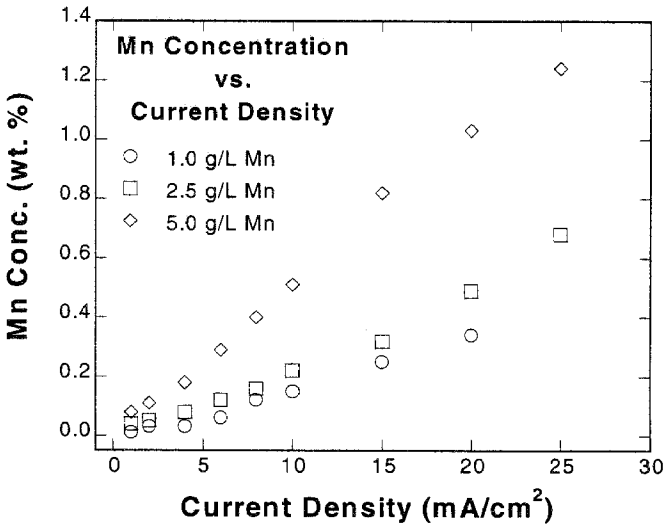

Figure 1. Dependence of alloy composition on dc deposition current density. A conventional Hull cell was used to plate several micrometers of material. Concentration was determined via WDS.

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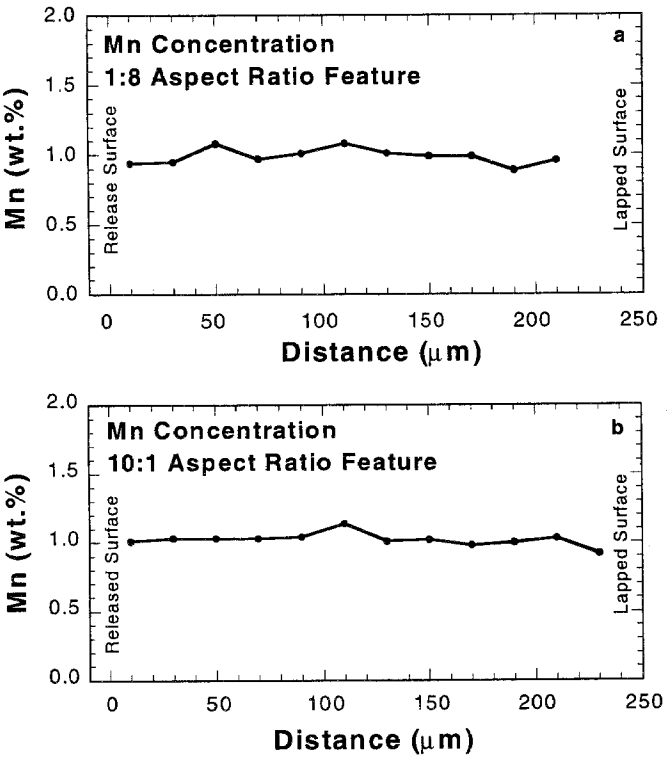

Figure 2. Alloy composition as a function of deposit thickness in (a) low and (b) high aspect ratio features. DC plated alloy has good compositional uniformity in both low and high aspect ratio features. The "release" surface corresponds to the substrate/film interface, while the "lapped" side corresponds to the top of the deposited film.

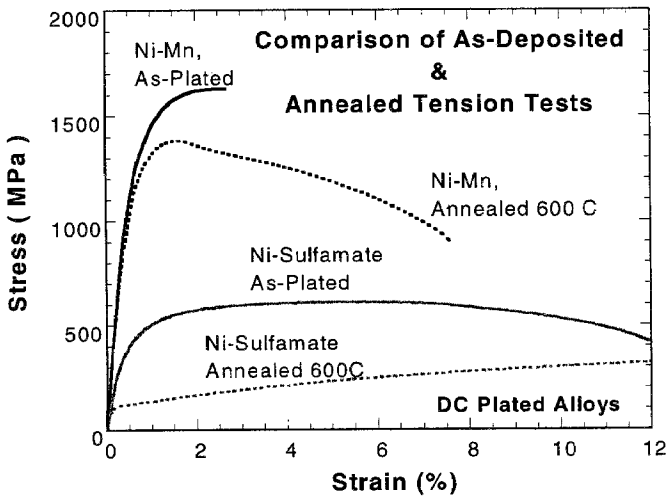

Figure 3. Tensile properties of as-plated dc electrodeposited NiMn alloy (at room temperature). Heat treating at 600°C for 1 h results in minimal loss in yield strength while greatly improving ductility. Tensile curves for as-plated and annealed pure Ni from a sulfmate bath are shown for comparison.

trolyte concentrations for dc experiments are indicated for each case. Pulse plated NiMn materials were produced with 0.5 g/L Mn and a two-step square waveform. In the first step of the waveform, a current density i_1 of 3 mA/cm^2 was applied for t_1 = 4.4 s, while for the second step i_2 = 15 mA/cm^2 and t_2 = 0.667 s. The choice of these parameters is discussed later.

Si wafers patterned with SU8 and metallized with Cu were used to define a miniature tensile test specimen geometry. The wafers were fixed to a plastic support where electrical contact was made to the working electrode lead and immersed in the electrolyte for deposition. Deposited wafers were lapped flat to 250 μm, after which the SU8 was mechanically removed from the Si substrate by crazing it in liquid nitrogen (it was verified with conventional Ni samples that this removal step had no effect on the mechanical properties of the deposited metal). The electrodeposited tensile test specimens were freed from the Si by dissolving the Cu metallization layer in a chemical etchant that does not attack Ni.

The tensile specimens patterned in the SU8 molds were simple "dog bone" geometries. The uniform gauge length measured 6 mm in length and 0.76 mm in width. Thickness of the specimens was defined by the lapped thickness of the wafer and was 0.25 mm (250 μm) as indicated above. Specimens were tested in uniaxial tension in an Instron model 5848 microtester. Load was measured using a 1 kN load cell and displacement was measured using a noncontacting laser extensometer (EIR model LE-01) having approximately 1 μm resolution. Tests were performed at room temperature at a constant extension rate of 3×10^{-3} mm/s.

Film stress was characterized using a bent strip stress analyzer (Specialty Testing and Development Co., PA). Approximately 1-2 μm of metal were deposited on a bent strip copper beryllium alloy substrate. Film stress values usually saturate after the first micrometer of deposited Ni, so thickness artifacts were minimized.[7] The average value of several experiments was taken for each case, with error bars showing the standard deviation of the measurements.

Results and Discussion

DC plated NiMn.—The effect of current density and Mn loading in the electrolyte on Mn content in the deposits was investigated using a conventional Hull cell at 28 ± 2°C. Figure 1 shows the results for both current density and bath concentration. Mn content in the alloy increased monotonically with increasing current density for all bath compositions examined. Increased Mn loading in the electrolyte resulted in generally higher levels in the deposit. These results are in good agreement with previous results for dc deposition.[13]

While the effect of transport was not explicitly characterized, the Ni to Mn mass ratios in the deposited metal and electrolyte are roughly equal (about 0.5-1%), suggesting that the deposition is not of the anomalous type for the conditions in the current study.[12,16] Because manganese is not being consumed at a rapid rate at the cathode, one expects that the Mn content is not excessively sensitive

Table I. Summary of mechanical properties for electrodeposited materials.

Alloy	Condition	σ_y (MPa)	UTS (MPa)	ε_{unif} (%)	ε_{frac} (%)
Ni-sulfamate	As-plated	385	610	5.5	12.8
Ni-sulfamate	Annealed 600°C	85	420	32	>40
NiMn (dc-plated)	As-plated	1250	1630	2.5	2.5
NiMn (dc-plated)	Annealed 600°C	1200	1350	1.2	7.5
NiMn (pulse plated)	As-plated	860	1125	2.9	5.8
NiMn (pulse plated)	Annealed 600°C	740	840	2.6	9.5

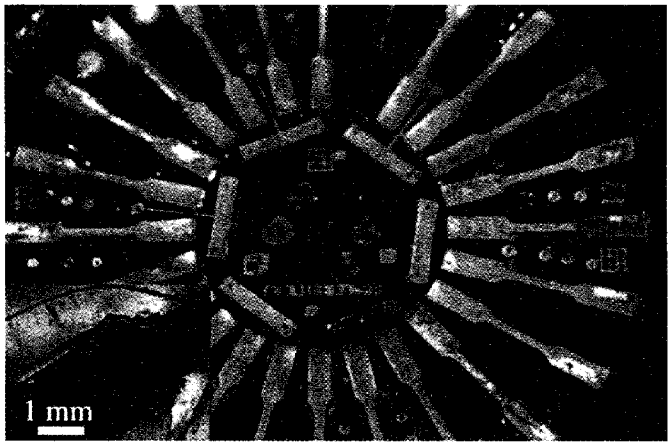

Figure 4. Failure of a HARMST mold results from excessively high stresses for dc-plated NiMn alloy. Electrolyte had 5 g/L Mn; film deposited at a current density of 7 mA/cm^2. Cracking in the polymer resist material and in the alloy itself is evident. The large photo shows the specimen pattern layout, approximately 6 cm across. The inset is a close-up with the scale indicated.

to mixing conditions. This is important for through-mask electrodeposition, where various aspect ratio features in the insulating mask may occur.

Such behavior is in contrast to other electrodeposited alloy systems where anomalous codeposition occurs. For example, typical NiFe and NiCo baths have concentrations of Fe or Co similar to that of the Mn considered here, but resulting deposits have as much as 20-30 wt % Fe or Co.[12,16] For NiCo, significant gradients in Co concentration and mechanical properties have been noted in high aspect ratio features due to Co ion transport limitations and its depletion at the bottom of such features.[17]

Because the consequences can be severe, the transport effects on compositional uniformity of the present alloy system were carefully characterized. Figure 2 shows the composition of a NiMn alloy as a function of feature depth for low and high aspect ratio structures, respectively (a low aspect ratio feature being one that is wide relative to its depth). The term "release surface" in Fig. 2 refers to the film/substrate interface. This is therefore the bottom surface of the deep mold features. Similarly, the term "lapped surface" refers to the final top surface of the mold that is mechanically ground and polished prior to the removal of the individual parts from the wafer.

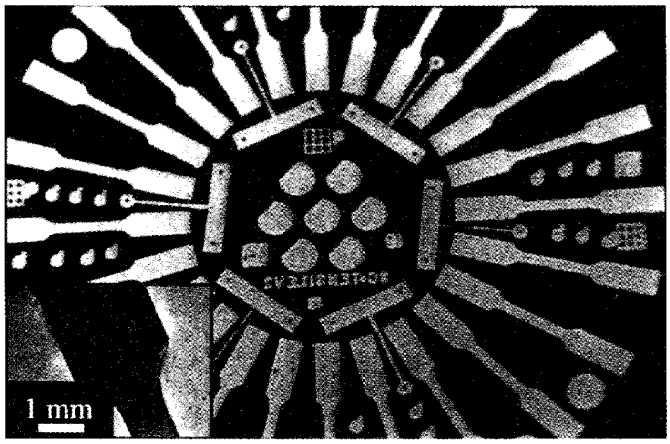

Figure 5. Successful deposition of specimens in a HARMST mold indicates low overall stress in deposit. There is no evidence of cracking in the polymer molding material or in the electrodeposit itself. The large photo shows the specimen pattern layout, approximately 6 cm across. The inset is a close-up with the scale indicated.

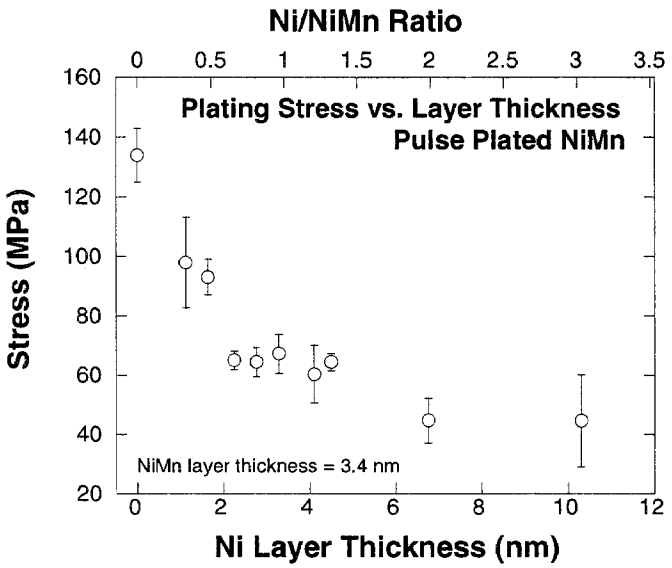

Figure 6. Residual stress of the pulse plated NiMn as a function of the calculated Ni layer thickness. The calculated NiMn layer thickness is fixed at 3.4 nm. The top scale shows the Ni to NiMn layer thickness ratio. As the Ni spacer layer thickness reaches that of the NiMn, stress falls and eventually plateaus.

The composition [determined through wavelength dispersive spectroscopy (WDS)] is similar for both aspect ratios as well as being uniform through the deposit thickness. Therefore, we can conclude that the different mixing conditions in the two microfeatures do not have a large effect on the alloy composition. Thus, the application of the current electrodeposition process to through-mask plating is greatly simplified.

Figure 3 shows a stress-strain curve of a tensile test specimen deposited from a Ni sulfamate electrolyte with 5 g/L Mn at 7 mA/cm^2 and 28°C under dc plating conditions. The alloy contains approximately 1 wt % Mn. A second curve shows the stress-strain behavior after a 1 h anneal at 600°C. Ductility is improved, with little loss in yield strength. A reference curve of pure Ni from a sulfamate bath without Mn is shown for comparison. Upon heat

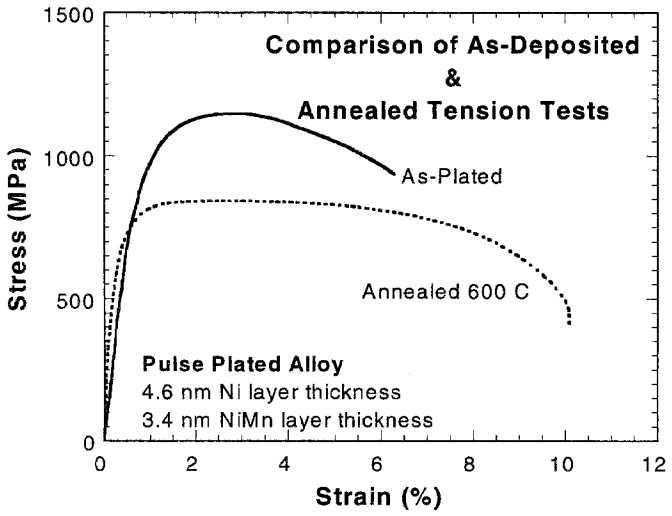

Figure 7. Tensile properties of pulse plated NiMn alloy (at room temperature). Ductility of as-plated alloy is improved over that shown in Fig. 3 for the dc-plated alloy, with only a small loss in yield strength. Postannealing strength is reduced by about 15% but is still much higher than that of the unalloyed Ni shown in Fig. 3.

treating, the pure Ni loses most of its strength. The strength retention of the NiMn alloy is comparable to that of some wrought superalloys, as has been reported previously.[14] This material seems ideal for high performance actuator applications. These and additional mechanical property measurements to be discussed subsequently are summarized in Table I.

While specimens can be electrodeposited in relatively thin sections under dc plating conditions near room temperature, as the deposit thickness increases, plating stresses become problematic. It is possible to lower plating stresses of Ni deposited from a sulfamate electrolyte by plating at higher bath temperatures.[8] But plating processes for precision HARMST applications generally are restricted to near ambient temperatures due to thermal expansion effects of the polymer molding material (PMMA, SU8, etc.).[18] At 28°C, a temperature we have found minimizes dimensional distortions in the polymer mold, residual stresses in the dc-plated NiMn alloy are sufficient to cause warpage of the metal, as well as failure of the polymer molding material. The problematic nature of thick section deposition at this temperature is directly the result of plating-induced stresses, and the consequences of these stresses are shown in Fig. 4 (a tensile bar mold dc-plated with the NiMn alloy). Here, the plating stresses were so high that the molding polymer failed. In some locations, the deposit itself cracked, rendering the part unusable. Thus, while the alloy has properties that clearly recommend it for use in microsystem applications, the inability to fabricate deposits of reasonable thicknesses precludes the use of the dc plated material. Our further attempts at varying Mn electrolyte content and current density with dc-plating processes to arrive at a strong ($\sigma_y > \sim 800$ MPa), low stress alloy were unsuccessful.

Pulse plated NiMn.—Figure 1 shows that the Mn composition of the alloy is a strong function of the current density and that careful control of the current could be employed to tailor the composition in a favorable way. Considering the behavior observed in Fig. 1, it was postulated residual stress could be moderated by nanostructuring the alloy; thin regions of relatively pure, low stress (and low strength) Ni could be deposited at lower current densities, with higher strength, stressed NiMn alloy regions deposited at higher current densities. Our expectation was that the low strength Ni regions could deform sufficiently to accommodate the plating stresses of the high stress NiMn regions. This approach is somewhat different than multilayer alloys considered previously;[19] in our case, the less noble metal is present in low concentrations. Moreover, our intention is not to derive strength from the high interfacial area, but rather to lower residual stresses to manageable levels by interspersing low stress metal in between high strength but highly stressed NiMn.

The approach was shown to be successful. Figure 5 shows the pulse plated material in an identical mold to that shown in Fig. 4. Stresses are remarkably lower than in the previous figure. The molding polymer is free of any cracking, and the plated features are well formed and free of damage. Plating-stresses have been quantified, and Fig. 6 shows the residual stress as a function of the soft Ni spacer layer thickness. After the Ni layer attains the calculated thickness of the NiMn layer, stresses plateau. Pure Ni from a sulfamate bath is typically 0 to 10 MPa tensile at 28°C. In our experience, film stresses greater than about 70 MPa are usually sufficient to cause film delamination or fail the substrate.

Figure 7 shows the stress-strain behavior of the pulse-plated alloy. These plating conditions were selected to yield a structure consisting of alternating regions of Ni and NiMn 4.6 and 3.4 nm thick, respectively. While not as strong as the material in Fig. 2, its strength is still much higher than that of pure Ni. Yield strength subsequent to a 1 h anneal a 600°C was reduced by only about 15% compared to about an 80% loss for Ni sulfamate. These data are summarized in Table I.

A preliminary investigation of the microstructure shows that the NiMn material has a smaller average grain size than pure Ni deposited from a sulfamate bath without Mn (about 0.25-0.50 μm *vs.* 2 μm, respectively), which is principally responsible for its higher yield strength.[20] Annealed NiMn samples show only a small amount of grain growth, explaining the strength retention with annealing. The mechanism by which the small amount of codeposited Mn impedes grain growth is still unclear and is currently being studied.

Conclusions

Depositing a NiMn alloy as a compositionally modulated film via pulse plating is shown to be an effective way to mediate plating stresses. The deposition process employed was developed to produce a compositionally modulated NiMn alloy consisting of alternating Ni and NiMn regions, 4.6 and 3.4 nm thick, respectively. The resulting alloy exhibits high strength, good ductility, and low plating stress as manifested in the successful fabrication of thick section deposits. The material shows only a small loss of yield strength with 1 h anneals up to 600°C due to impeded grain growth. The composition of the alloy is uniform, even for features having very different aspect ratios, as commonly found in resist masks used to define HARMST.

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List of Symbols

i_1 current density 1, mA/cm^2
i_2 current density 2, mA/cm^2
t_1 pulse time 1, s
t_2 pulse time 2, s
ε engineering strain, %
σ_y engineering yield stress, MPa

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